Introduction to Plane-Wave Basis Sets and Pseudopotential Theory

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Kohn-Sham Equations

▶ Nonlinear eigenvalue equations

$$\left(-\frac{1}{2}\nabla^2 + \upsilon_{ion} + \upsilon_H[n] + \upsilon_{xc}[n] \right)\psi_i = e_i\psi_i$$

$$n(r) = \sum_{i=1}^{N} \left|\psi_i\right|^2$$

▶ Require self-consistent solution

▶ In order to solve these equations we need to expand the wavefunctions Ψ in a basis set

$$\psi_i = \sum_{\alpha} c_\alpha \varphi_\alpha$$

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Gaussian DFT Versus Plane-Wave DFT

Gaussian Basis Set

▶ Parallel Efficient

▶ All-Electron

- Core regions included in calculation
- First row transition metals can readily be calculated

▶ Ab Initio MD expensive

- Pulay forces

▶ Different basis sets for molecules and solids

PlaneWave Basis Set

▶ Parallel Efficient

▶ Requires pseudopotentials to be efficient

- Not all-electron
- Core region not included
- First row transition metals are difficult
  - Norm-conserving pseudopotentials of the nodeless 3d states require large plane-wave basis sets
  - Significant overlap between the valence 3d states and core densities

▶ Efficient Ab Initio MD

- Car-Parrinello

▶ Same basis set for molecules and solids

Plane-Wave Basis Sets
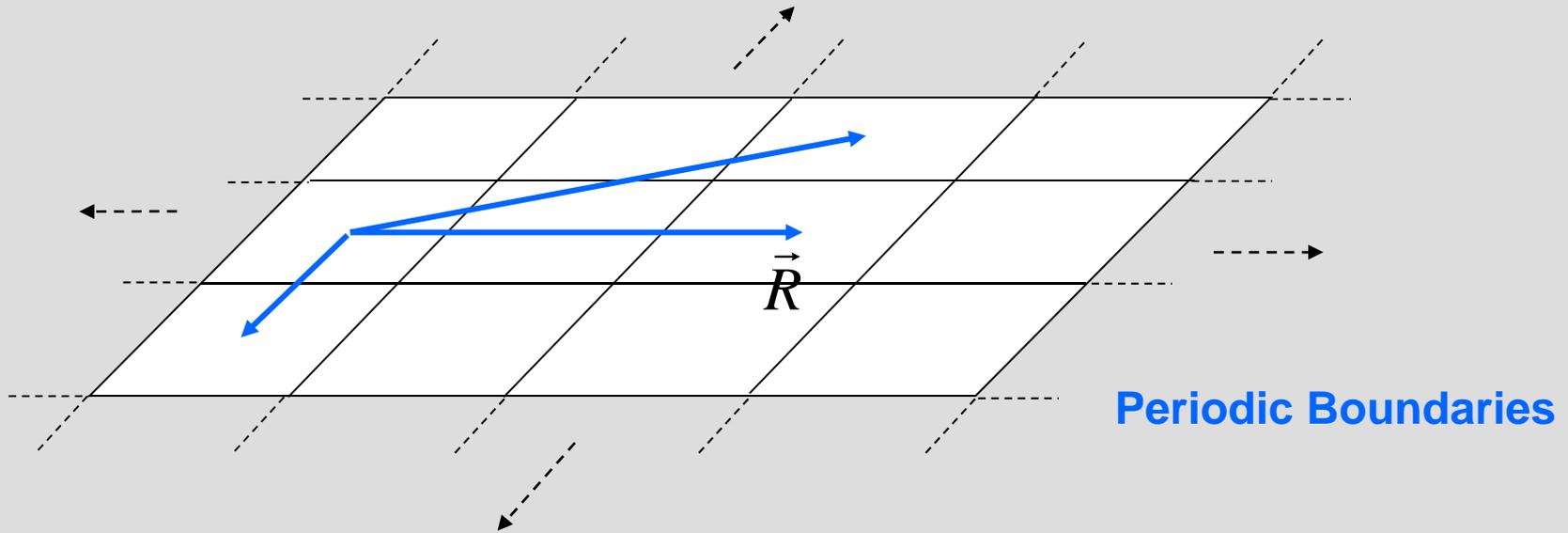
System is assumed to be placed inside a unit cell defined by the unit vectors
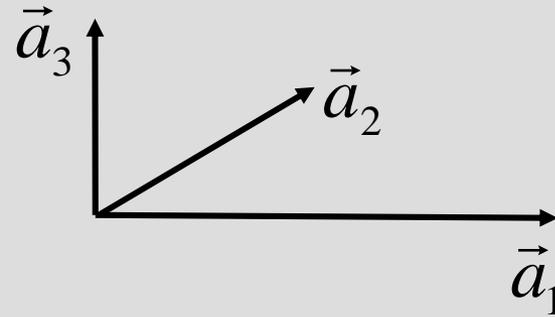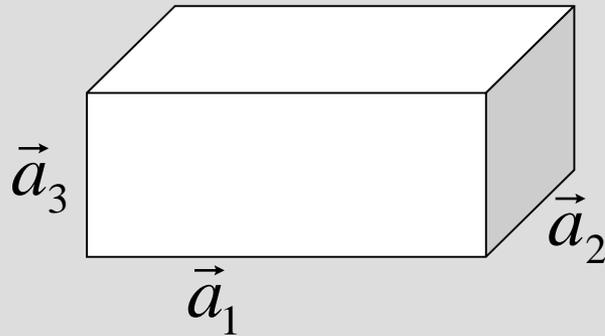
The volume of the unit cell is

$$\Omega = \left[\vec{a}_1, \vec{a}_2, \vec{a}_3\right] = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

Plane-Wave Basis Sets

Periodic Boundaries

$$\vec{r} \rightarrow \vec{r} + \vec{R}$$

where

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, \qquad n_1, n_2, n_3 = \text{integers}$$

Plane-Wave Basis Sets

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Plane-wave Expansion

Since are system is periodic our plane-wave expansion must consist of only the plane-waves $e^{i\vec{G}\cdot\vec{r}}$ that have the periodicity of the lattice,

We can determine these plane-waves from the following constraint

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}$$

Plane-Wave Basis Sets

It is easy to show from the periodicity constraint that the wave-vectors can be defined in terms of the following reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega}$$ Reciprocal lattice vectors

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega}$$

Wave-vectors that satisfy the periodicity of the lattice

$$\vec{G}_{i_1 i_2 i_3} = \left(i_1 - \frac{N_1}{2} \right)\vec{b}_1 + \left(i_2 - \frac{N_2}{2} \right)\vec{b}_2 + \left(i_3 - \frac{N_3}{2} \right)\vec{b}_3$$

Plane-Wave Basis Sets

The exact form of the plane-wave expansion used in plane-wave code is

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{i_1=1}^{N_1} \sum_{i_2=1}^{N_2} \sum_{i_3=1}^{N_3} \tilde{u}_n\left(\vec{G}_{i_1 i_2 i_3}\right) e^{i\vec{G}_{i_1 i_2 i_3} \cdot \vec{r}}$$

The upper-limits of the summation (N_1,N_2,N_3) control the spacing of the real-space grid

$$\vec{r}_{i_1 i_2 i_3} = \left(\frac{i_1}{N_1} - \tfrac{1}{2}\right)\vec{a}_1 + \left(\frac{i_2}{N_2} - \tfrac{1}{2}\right)\vec{a}_2 + \left(\frac{i_3}{N_3} - \tfrac{1}{2}\right)\vec{a}_3$$

Plane-Wave Basis Sets

There is a further truncation of plane wave expansion in plane-wave calculations. Namely, only the reciprocal lattice vectors whose kinetic energy lower than a predefined maximum cutoff energy,

$$\frac{1}{2}\left|\vec{G}\right|^2 < E_{cut}$$ Wavefunction Cutoff Energy

are kept in the expansion, while the rest of the coefficients are set to zero. Besides reducing the computational load, this truncation strategy limits the effects of unit cell orientation on the outcome of the calculation.

DFT calculations rarely use a completely converged plane-wave basis, but that convergence is usually unnecessary. However, incomplete basis set calculations using different cell sizes require that each calculation use the same E_{cut}

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Plane-Wave Basis Sets

Since the density is the square of the wavefunctions, it can vary twice as rapidly. Hence for translational symmetry to be formally maintained the density, which is also expanded using plane-waves
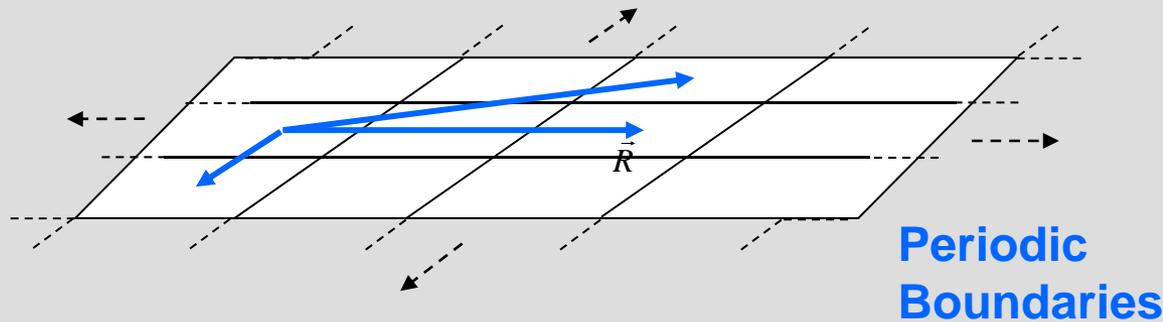
$$\rho(\vec{r}) = \sum_{n} u_n^*(\vec{r}) u_n(\vec{r}) = \sum_{\vec{G}} \tilde{\rho}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Should contain 8 times more plane-waves than the corresponding wavefunction expansion

$$\frac{1}{2}\left|\vec{G}\right|^2 < 4E_{cut}$$ Density   Cutoff Energy

Often the Density cutoff energy is chosen to be the same as the wavefunction cutoff energy – This approximation is known as dualling

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Plane-Wave Basis Sets

Periodic Boundaries

In solid-state systems, the plane-wave expansion given by

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$ Γ–point Plane-wave Expansion

is not complete. Based on the fact that the translation operators T(R) are compatible with the Hamiltonian of the system, [T(R),H]=0, and that not all eigenkets of T(R) can be expanded strictly in terms of the set of eigenkets |u$_n$>. The wavefunction expansion can be generalized

$$\left|\vec{k},n\right\rangle = \left|\vec{k}\right\rangle\left|u_n\right\rangle \quad \text{or} \quad \psi_{\vec{k},n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_n(\vec{r})$$ Bloch's Theorem

Where ***k*** are all the allowed wave-vectors in the primitive cell of the reciprocal lattice.

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Motivations for Pseudopotential Method

Valence wavefunction behavior in a typical molecular system
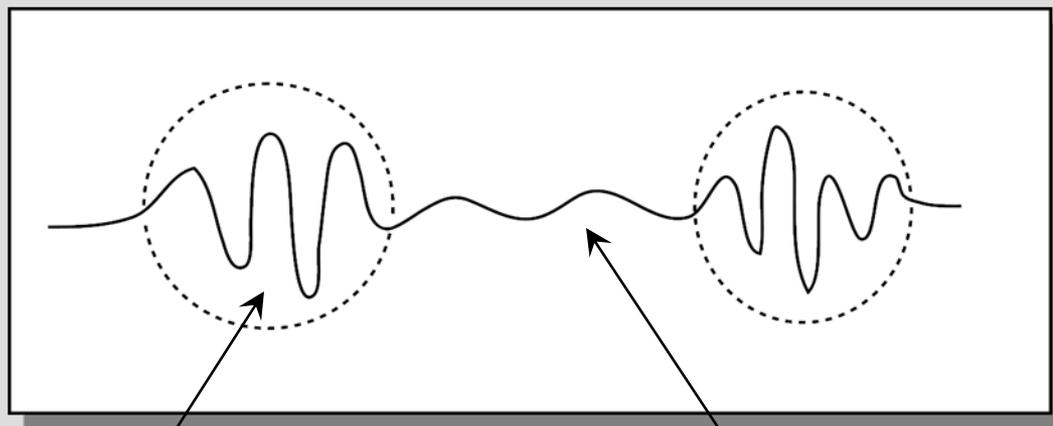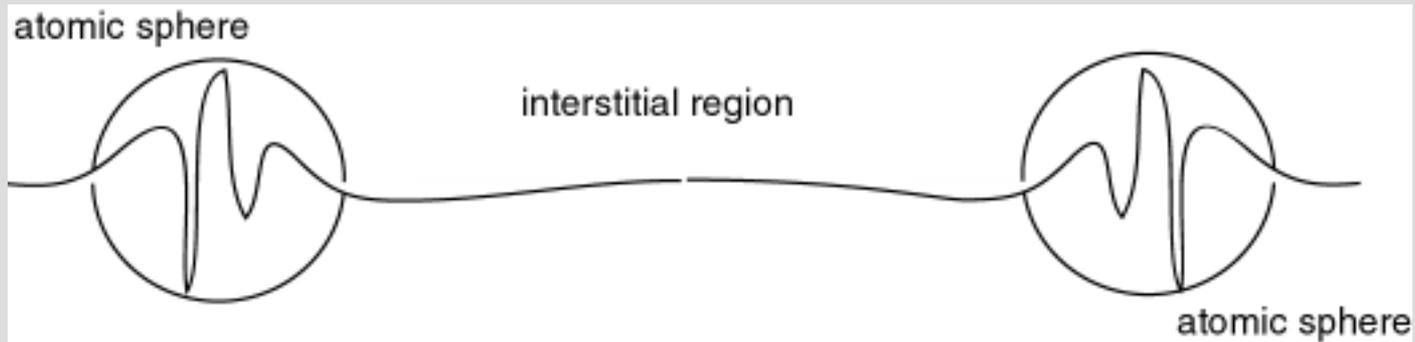

Atomic sphere region:

$$\sum_{\alpha} c_{\alpha} \varphi_{\alpha}(r)$$

Interstitial region:

$$\sum_{k} c_{k} e^{ik_{\alpha}r}$$

Pseudopotential Method

Valence wavefunctions can be divided into two regions

atomic sphere

interstitial region

atomic sphere

OPW

$$\left|\psi^v\right\rangle = \left|\widetilde{\psi}^v\right\rangle - \sum_c \left|c\right\rangle\left\langle c\left|\widetilde{\psi}^v\right\rangle\right.$$

$$H\left|\psi^v\right\rangle = E_v\left|\psi^v\right\rangle$$

Pseudopotentials

$$\left(H + V^R\right)\left|\widetilde{\psi}^v\right\rangle = E_v\left|\widetilde{\psi}^v\right\rangle$$

$$V^R\left|\widetilde{\psi}^v\right\rangle = \sum_c \left(E_v - E_c\right)\left|c\right\rangle\left\langle c\left|\widetilde{\psi}^v\right\rangle\right.$$

k

k
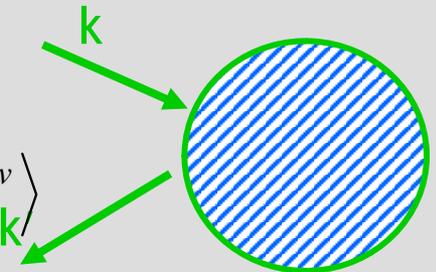
- Core electrons removed
- Strong ionic potential is replaced by a weak pseudopotential
- Valence electrons are described via a smooth pseudowavefunctions
- Loss of wavefunction in core region
- 3d valence states are not well screened

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Pseudopotential Method

The pseudopotential method is based on two observations. **First**, in almost any system one could identify a set of the so-called core orbitals which change little from their atomic counterparts. **Second**, the remainder, the so-called valence orbitals, acquire their oscillating behavior mainly due to Pauli exclusion principle or, in plain words, orthogonality constraints to the core orbitals. In pseudopotential approximation the original atoms that constitute a given chemical system are modified by removing core energy levels and enforcing the Pauli exclusion principle via repulsive pseudopotential. This removes the wiggles from the atomic valence orbitals and allows efficient application of plane wave basis set expansion. The resulting pseudoatoms will in general acquire a nonlocal potential term.

$$V\left(\vec{k},\vec{k}'\right)\left|\vec{k}\right\rangle = \left|\overleftarrow{k}'\right\rangle$$

k

k'
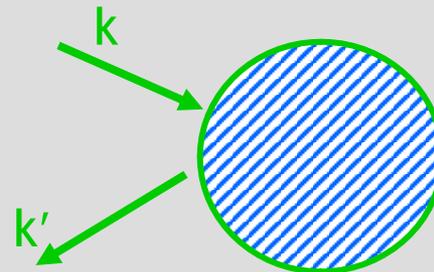
Pseudopotential Method

► There are many other ways to define V^R such that $H+V^R$ has the same valence eigenvalues as the actual Hamiltonian.

► Hamann et al proposed a simple procedure to extract pseudopotentials from atomic calculations, these potentials are designed to have the following properties:

- Real and pseudo valence eigenvalues agree for a chosen "prototype" atomic configuration
- Real and pseudo atomic valence wavefunctions agree beyond a chosen "core radius" r_c
- Real and pseudo valence charge densities agree for $r > r_c$
- Logarithmic derivatives and the first energy derivatives agree for $r > r_c$

► This class of pseudopotentials are called norm-conserving pseudopotentials

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Constructing a Pseudopotential

Step 1: Solve all-electron eigenvalues and wavefunctions for a reference atom

Step 2: Construct pseudo wavefunction from the all-electron wavefunctions, such that:

- Real and pseudo eigenvalues agree
- Real and pseudo atomic valence wavefunctions agree beyond a chosen "core radius" rc
- Real and pseudo valence charge densities agree for r>rc
- Logarithmic derivatives and the first energy derivatives agree for r>rc

Step 3: Invert the atomic Schrodinger Equation to obtain a screened pseudopotential

Step 4: Generate an ionic pseudopotential from the screened pseudopotentials

Step 5: Transform the semi-local potential to a non-local form (Kleinman-Bylander)

Free-space Boundary Conditions

$$E_{e-e} = \frac{1}{2} \iint_{\Omega} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

Figure: accuracy of free-space methods

- Technique to implement free-space boundary conditions into plane-wave methods

  - E.J. Bylaska et al, J.Phys.Chem, 100, 6966 (1996).

  - E.J. Bylaska et al, Comp. Phys. Comm.

- Allows us to calculate charged systems

- Implementing Free-Space boundary condition does not significantly degrade performance of plane-wave codes.
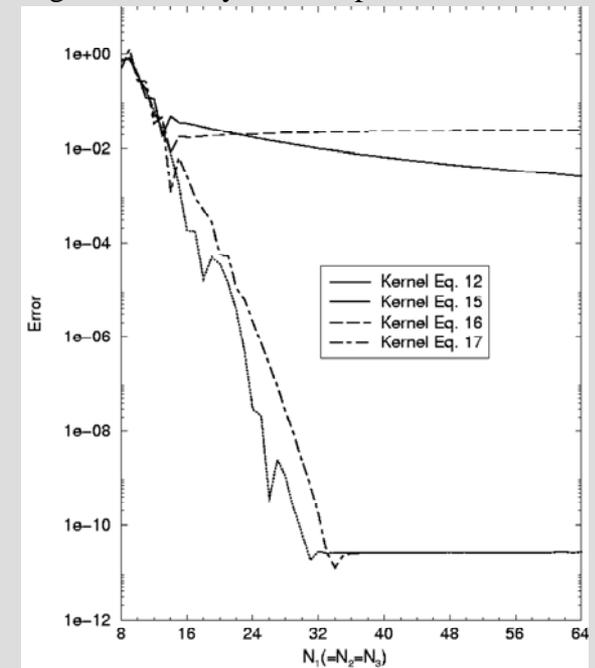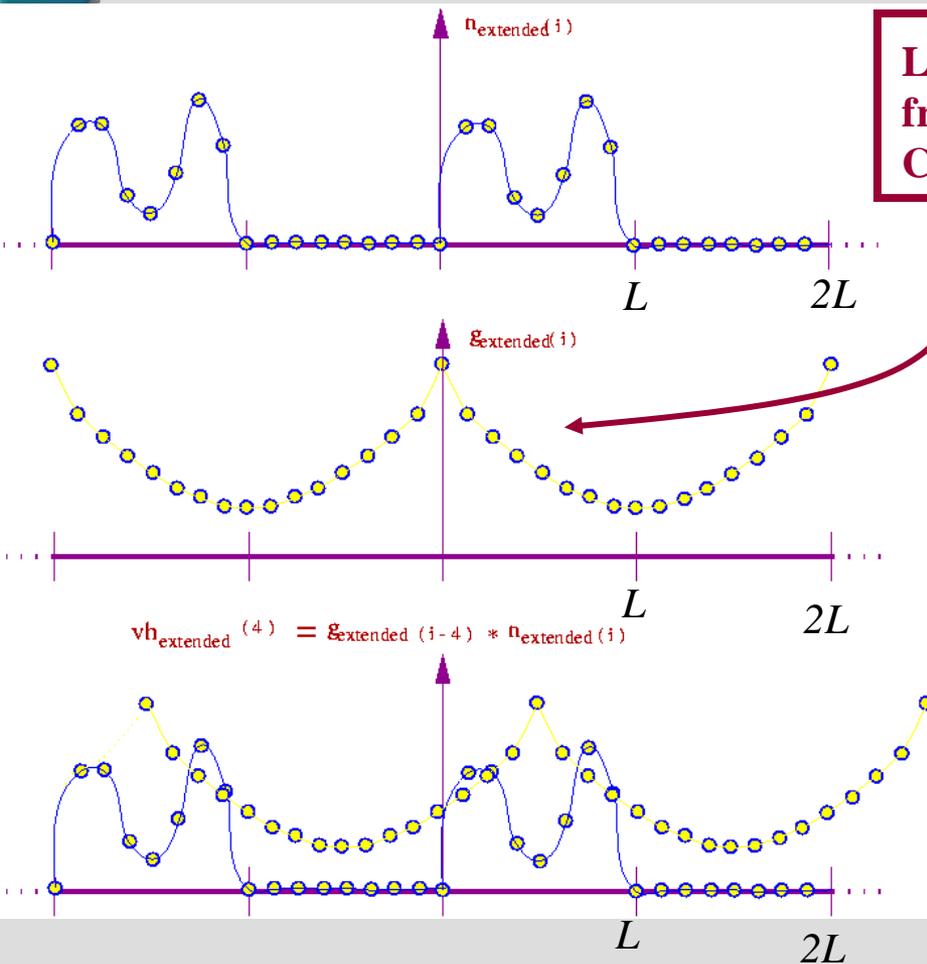
- Technique implemented into PAW code.

Table 3: Fe^{3+} multiplet structure

	PAW/101Ry	NWChem/VTZ	PSPW/131Ry	CAS(5e,5d)/ecdp	Exp.
^4X-^6X	3.3 eV	3.0 eV	6.2 eV**	4.6eV	4.1eV
^2X-^6X	4.8 eV	4.6 eV	9.1 eV**	6.6eV	

** semi-core corrections not included.

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Aperiodic Convolution: Working in the $[-L,L)^3$ domain

Lack of accuracy comes from cusp in cutoff Coulomb kernel

Cutoff Coulomb Kernel

$$g(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} g_a(\mathbf{G}) e^{i\mathbf{G}\bullet\mathbf{r}} & \text{for } |\mathbf{r}| \leq R_{max} - \delta \\ \dfrac{1}{|\mathbf{r}|} & \text{otherwise} \end{cases}$$

$$g_a(\mathbf{G}) = \begin{cases} \dfrac{2\pi(R_{max})^2}{h^3} & \text{for } |\mathbf{G}| = 0 \\ \dfrac{4\pi}{h^3|\mathbf{G}|^2}\left(1 - cos\left(|\mathbf{G}|^2 R_{max}\right)\right) & \text{otherwise} \end{cases}$$

$$R_{max} = \begin{cases} L & (\text{simple cubic}) \\ \dfrac{\sqrt{2}}{2}L & (\text{face - centered cubic}) \\ \dfrac{\sqrt{3}}{2}L & (\text{body - centered cubic}) \end{cases}$$

$\delta = \text{small constant}$

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